# CEMENT AND LIME

## MANUFACTURE

# The Determination of the Proportions of Concrete.

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SOME known methods of determining the amount of cement in a sample of mixed concrete, such as the method specified by the American Society for Testing Materials (C85–42), involve the estimation of the amount of lime or silica, and necessitate the separation of the coarse and fine materials by wet sieving, and the evaporation of the excess water from the fine material. Since a large volume of water is required for efficient sieving, evaporation takes some time, and the subsequent chemical analysis is laborious especially if the aggregate contains lime. The method described in this article avoids the necessity of evaporating large quantities of water. The basis of the method is the determination of the specific gravity, by a hydrometer, of a suspension in water of the material passing a 100-mesh sieve. The hydrometer is preferred to weighing because of the cost and difficulty of obtaining a balance having sufficient capacity and accuracy to determine small differences in weight. The tests can be made at the site of the works where the concrete is made. When the concrete is made from clean aggregate without particles passing a B.S. sieve No. 100 the method of determination of the proportions is as described in the following.

A sample of wet concrete weighing about 3 kg. is washed on B.S. sieves Nos. 14 and 100, the purpose of the coarser sieve, which is used first, being to protect the No. 100 sieve from damage. The aggregate retained on the No. 100 sieve is dried and weighed, and a complete grading analysis is made. The cement, which passes the No. 100 sieve, is collected in a large metal cylinder and water is added to make up a known volume. The writer uses a metal cylinder having a capacity of 19 litres when filled to $\frac{1}{4}$ in. below the brim. After vigorously stirring with a wooden paddle for 1 minute, a hydrometer of the type shown in *Fig.* 1 is inserted and readings are taken at intervals of 10 seconds for $1\frac{1}{2}$ to 2 minutes. The water with the suspended material is restirred and the hydrometer reading retaken. This process is repeated until four series of readings have been obtained. A hydro-

meter reading is also taken of the water used for washing, and any necessary correction for temperature is made.

The hydrometer readings are then plotted against time as in *Fig.* 3 and the curves extrapolated to zero on the time scale as shown. The average value of the four series at zero is calculated, and by reference to a control curve, such as that in *Fig.* 2, the amount of cement is determined. The control curve is obtained by taking hydrometer readings of water in which is suspended known quantities of cement similar to that used in the concrete.
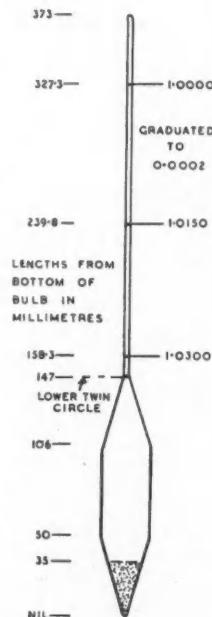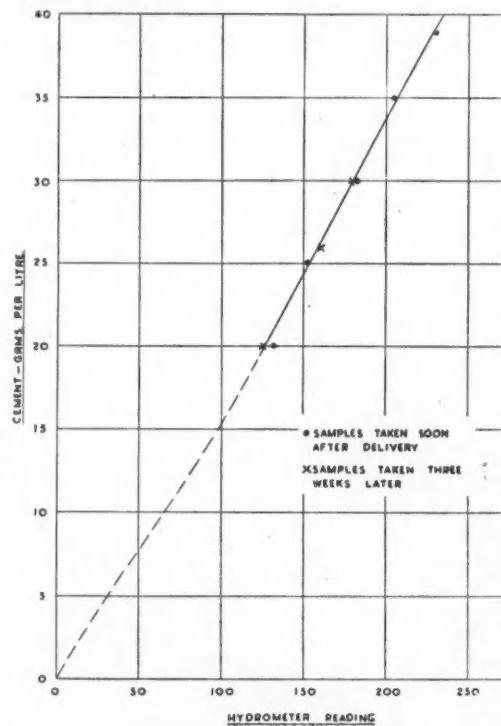
Fig. 1.—Hydrometer.          Fig. 2.—Control Curve for Cement.

If the aggregate contains fine material passing a No. 100 sieve it is necessary to adopt one of two courses. (1) If the quantity of dust is small and uniformly dispersed, the quantity contained in the sample can be estimated. This dust increases the specific gravity of the suspension and a correction is made when determining the cement content. In this determination allowance is made for the difference in specific gravities of the dust in the aggregate and the cement. (2) If the quantity of dust is unknown, or if a more accurate determination than given by (1) is required, some of the water with the material in suspension, as used for

the hydrometer readings, is treated with hydrochloric acid in the following manner. Immediately after being vigorously stirred, a sample of the water is obtained by a 50-ml. pipettte and transferred to a beaker. The cement and any soluble grains of dust are then dissolved in hydrochloric acid. The insoluble residue
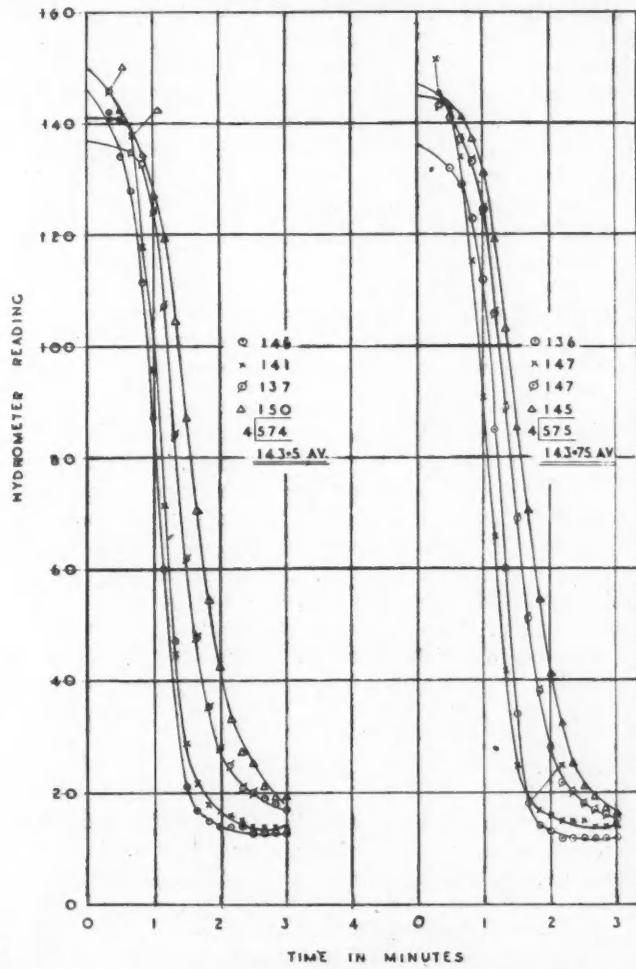


Fig. 3.—Hydrometer Readings for Cement in Suspension.

remaining is filtered and weighed. A deduction can then be made for the amount of dust as described later, and the quantity of cement can be determined. For this test chemical apparatus and an accurate balance are necessary, so that the method is not generally suitable for use at the site.

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## Experimental Verification.

*Fig.* 3 shows examples of the curves, obtained by plotting hydrometer readings against the time elapsing after mixing, during early investigations of the proposed method. The curves apply to the same batch of cement after mixing to ensure uniformity. Each of the two series of curves applies to repeat tests with 25 g. of cement per litre. Other tests were made with 30 g. per litre. Although the shapes of the curves vary, the average of the four values when the curves are extrapolated to zero on the time scale are in close agreement. The curves tend to become horizontal after three to four minutes and the amount of cement was found to affect the hydrometer reading at this stage also. The indication was, however, not so reliable and in later tests the hydrometer readings were taken for the first $1\frac{1}{2}$ or 2 minutes only. The accuracy of the extrapolation is increased if as many readings as practicable are taken during the first half-minute. An example of a control curve plotted from tests using quantities of cement varying from 20 g. to 40 g. per litre is given in *Fig.* 2. In other tests it was observed that the accuracy of the results of repeated tests decreased for quantities of cement exceeding 40 g. per litre. In the tests described later the quantity of mixed concrete was selected to give a cement content of between 20 g. and 35 g. per litre.

### Effect of Dust Passing 100-mesh Sieve.

Dust passing a 100-mesh sieve affects the specific gravity of the water with material in suspension in a similar manner to cement. The specific gravity of the dust is, however, about 2·65 compared with 3·15 for cement. Therefore the hydrometer reading would be expected to be only 2·65 ÷ 3·15 times that for the same weight of cement. This was verified by making tests using mixtures of cement and dust in different proportions. Curves for mixtures of dust and the cement to which the control curve in *Fig.* 2 applies are given in *Fig.* 4 ; the curves (*a*) apply to 25 g. of cement plus 2·5 g. of dust per litre, and the curves (*b*) to 20 g. of cement plus 8 g. of dust per litre. Referring to *Fig.* 2, 25 g. of cement per litre are equivalent to a hydrometer reading of 152·5. Also 2·5 g. of dust are equivalent to $2\cdot5 \times \dfrac{2\cdot65}{3\cdot15} = 2\cdot1$ g. of cement which is equivalent to a hydrometer reading of 11.

Thus theoretically the hydrometer reading should be 152·5 plus 11 = 163·5, compared with the actual reading of 166 [*Fig.* 4(*a*)], the error being 1·5 per cent. A similar reference to *Fig.* 2 and calculation show that 20 g. of cement per litre are equivalent to a hydrometer reading of 128 and 8 g. of dust to a reading of 42, giving a theoretical reading of 170 compared with the actual reading of 164 [*Fig.* 4(*b*)], an error of 3·5 per cent.

An example of a calculation of the amount of dust in a sample is given in the following.

It is found by test that the insoluble residue after dissolving a sample of the cement alone in hydrochloric acid is 1·80 per cent. The insoluble residue after treating a sample of the dust from the aggregate with hydrochloric acid is 91·61 per cent. The insoluble residue after treating a mixture of cement and dust with

hydrochloric acid is 59·6 per cent. If the mixture contains $x$ per cent. of cement and $y$ per cent. of dust, then (1) $x + y = 100$; (2) $\dfrac{1\cdot80x}{100} + \dfrac{91\cdot61y}{100} = 59\cdot60$, and (3) $0\cdot0197x + y = 65\cdot2$. By subtracting (3) from (1) $0\cdot98x = 34\cdot8$, and therefore $x$ is 35·5. Thus the calculated proportions of cement and dust are 35·5 per cent. and 64·5 per cent. respectively. The quantities used in the test to which the foregoing calculations apply were 33·3 per cent. of cement and 66·7 per cent. of
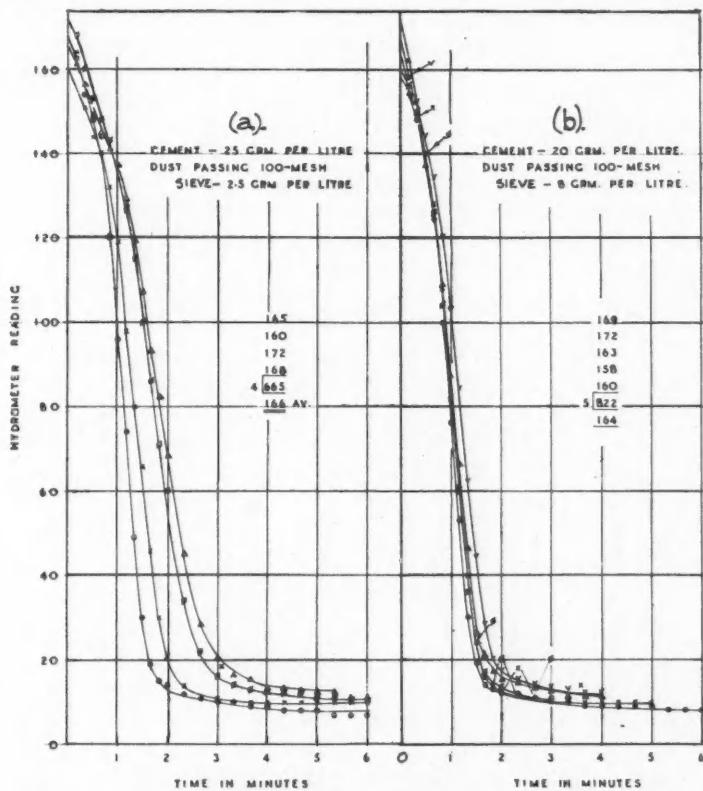


Fig. 4.—Hydrometer Readings for a Mixture of Cement and Dust.

dust, so that the error in the cement content is 2·2 per cent. The quantity of dust used in the test was more than commonly occurs and the degree of error is therefore thought to be the greatest likely to occur.

### Accuracy of the Determinations.

To verify the accuracy of the method tests were made using cement alone, cement and dust, and a mixture of cement, sand, gravel and water in known

proportions.   The greatest error in the amount of cement found in more than
70 determinations was $\pm$ 4 per cent.   Thus if a concrete contains 20 per cent.
of cement by weight, the greatest error expected is 0·8 per cent., the probable
proportion of cement being therefore between 19·2 to 20·8 per cent.

## Water-Cement Ratio.

Having determined the weight of dried aggregate retained on a 100-mesh
sieve, the weight of cement, and the weight of dust passing a 100-mesh sieve,
the total weight of water in a concrete is the difference between the sum of the
foregoing weights and the total weight of the wet concrete.   An allowance must
be made for water absorbed by the aggregate.   The quantity of mixing water is
then the total weight of water less that absorbed by the aggregate, and the water-
cement ratio (by weight) is the weight of mixing water divided by the weight of
the cement.

## The Cement Industry in Finland.

A REPORT from the Commercial Secretariat of the British Legation at Helsinki
states that the firm of Pargas Kalkbergs Aktiebolag is the biggest producer of
cement in Finland with an annual output of about 250,000 tons of a total produc-
tion in the country of 500,000 tons.   The firm operates three kilns, and hopes to
install a fourth when it can be obtained.   The firm uses about 1½ tons of
limestone, 360 kilos of clay, 60 kilos of gypsum, and 250 kilos of coal to make one
ton of cement.   The coal is now being obtained from the United Kingdom and
Poland and the gypsum from Cyprus and French North Africa.   The kilns and
other heavy special machinery were supplied by F. L. Smidth of Copenhagen, and
the electrical machinery mainly by Strombergs, of Helsinki.   The company's lime
plant produces about 60,000 tons of lime a year.

## British Standards for Cements.

SINCE the publication of the revised British Standard No. 12 (1947) for ordinary
and rapid-hardening Portland cement, an alteration has been made to the clause
prohibiting the addition after burning of any materials other than calcium sulphate
or water; the term "calcium sulphate" has been replaced by "gypsum (or its
derivatives)."

# Rapid Analysis by Colorimetric Methods.

IT is an advantage in an industrial laboratory to reduce as much as possible the time taken for routine analyses. Recent research in Sweden has therefore been directed to determining reliable colorimetric methods for the quantitative analysis of siliceous materials such as cement clinker, kaolin, glass-wool, etc. The methods, which are described in a report* printed in the English language, apply to the determination of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, CaO, MgO, and $K_2O$. Different methods of analyses are discussed, and the high degree of accuracy of the results obtained by colorimetric analyses compared with those obtained from gravimetric analyses is established. The report shows that for cement clinker the average results obtained by the two methods and expressed as percentages to one decimal place (or to two decimal places in the case of $Na_2O$) were the same in the case of $Na_2O$, $SiO_2$, $TiO_2$, and MgO, and varied by 0·2 per cent. for $Fe_2O_3$, and by 0·1 per cent. for $Al_2O_3$, CaO and $K_2O$. None of the separate results on which the average values are based varied by more than 0·1 per cent. for cement clinker, while for the determination of $K_2O$ and $Na_2O$ the difference between the separate results did not exceed 0·01 per cent., and was frequently much less.

It is also shown that the complete analysis of a material to determine the
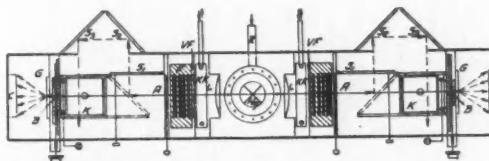


Fig. 1.—Arrangement of Colorimeter.

Hg, mercury discharge lamp.; R, air cooling coil; L, condenser lens; KK, cooling water cell; VF, heat filter; F, filter discs; A, shutter; $S_1$, movable mirror; $S_2$ and $S_3$, fixed mirrors; K, sample solution cell; B, graduated diaphragm; G, ground glass screen; C, photoelectric cell.

eight components mentioned, and including the preparation of three standard solutions and the calculation of the results, can be easily performed in a working day.

## Colorimeters.

A consideration of colorimetric apparatus is given, and a colorimeter (*Fig.* 1) designed at the Swedish Cement and Concrete Research Institute is described. The colorimeter consists of two identical symmetrical compartments. The measurement can therefore be made either with the aid of a calibration curve or directly by means of a reference solution. The lamp (Hg) which is directly connected to a 220-volt a.c. supply, is surrounded by a coil (R) which is perforated for additional air cooling of the lamp tube. The plano-convex lens (L) directs the rays into a parallel beam which passes through a rectangular glass cell (KK) filled with water and equipped with a cooling-water coil. This cell absorbs the

heat transmitted by conduction and radiation, the remainder of the radiant heat being absorbed by the heat filter (VF). After cooling, the light is rendered monochromatic by a series of glass filters (F), which are in a removable holder so that the filters and holder can be replaced at one time ; thus the filters need not be picked out separately. To protect the photoelectric cells from fatigue in the intervals between measurements without switching off the lamp, a screen (A) is fitted behind the filters. As the thermal equilibrium need not be disturbed and the filters need not be disarranged, the colorimeter is always ready for use.

A mirror ($S_1$), which can be moved to an angle of 45 deg., is mounted behind the screen. This mirror, in conjunction with the mirrors ($S_2$) and ($S_3$), can be used for deflecting the light beam so that it strikes the side wall of the glass cell (K). In colorimetric measurements the mirror ($S_1$) is pushed into the side wall of the colorimeter so as not to obstruct the passage of light through the cell (K) in the longitudinal direction. The transmitted or reflected light passes through an iris diaphragm (B) which is provided with a dial scale and is used for balancing the difference in voltage between the photoelectric cells. Finally, the light is diffused by the ground-glass screen (S) so that it strikes the surface of the photoelectric cell (C). The photoelectric cells are of the selenium barrier layer type, and are connected in a compensating circuit to a galvanometer used as a zero indicator.

The method of using the apparatus is, briefly, first to calibrate the colorimeter with solutions containing known concentrations of the test substance, a curve of the colorimeter readings and amounts of the test substance being plotted and corrected for the initial amount of the test substance in the solution. A solution containing the sample to be analysed is placed in the colorimeter and the reading taken ; the reading for the same reagent solution alone is then taken. The weights (in milligrammes) of the test substance corresponding to these two readings are read from the calibration curve and the difference is the weight of the test substance in the sample solution.

## Standard Solutions.

Brief directions for the preparation of the standard solutions required for the calibration of the colorimeter are given in the following.

SILICA.—About 1 g. of clean quartz sand is fused with sodium potassium carbonate. The melt is dissolved in about 250 ml. of water. The solution is filtered. A 100-ml. sample of the filtrate is taken for the gravimetric determination of $SiO_2$ by the generally-known method. After the solution has been analysed, a portion containing 100 mg. of silica is diluted in a 1,000-ml. graduated flask to about 750 ml. The solution is neutralized with hydrochloric acid to litmus paper and diluted to 1,000 ml. This solution contains 0·1 mg. of silica per ml.

ALUMINIUM.—From 2 g. to 3 g. of powdered aluminium are dissolved in hydrochloric acid. The solution is neutralized with sodium hydroxide and some NaOH is added in excess. Then the solution is boiled for five minutes and the precipitate is then filtered off. The filtrate is precipitated with colourless ammonium sulphite, boiled, and filtered. The filtrate is slightly acidified with hydrochloric acid and boiled until the smell of sulphuretted hydrogen has entirely disappeared. The

precipitated sulphur is filtered off. Aluminium is twice precipitated in the filtrate as hydroxide with ammonia. The precipitate is thoroughly washed and dissolved in 1,000 ml. of water. A 25-ml. to 50-ml. sample of this solution is taken for the gravimetric determination of aluminium. An aliquot part of the analysed solution is diluted so that the final solution contains 0·05 mg. of $Al_2O_3$ per ml.

IRON.—About 1 g. to 2 g. of iron-alum is dissolved in 100 ml. of hot water. The solution is filtered. The filtrate is strongly acidified with hydrochloric acid. A 10-ml. sample of the filtrate is taken for the determination of iron by titration. The analysed filtrate is diluted so as to obtain a solution containing 1·0 mg. of $Fe_2O_3$ per ml. This solution is used as stock solution. Directly before use the solution is diluted to 0·01 mg. of $Fe_2O_3$ per ml.

TITANIUM.—About 1 g. of titanium potassium fluoride is weighed into a platinum crucible. The fluoride is wetted with water and fumed off with concentrated sulphuric acid several times. The residue is dissolved in the least possible amount of sulphuric acid. The solution is diluted to 100 ml. and filtered. A 50-ml. sample of the filtrate is taken for the gravimetric determination of $TiO_2$. With the aid of the analysis, a portion of the filtrate containing 100 mg. of $TiO_2$ is diluted to 1,000 ml. so that the final solution contains 0·1 mg. of $TiO_2$ per ml.

CALCIUM.—About 5 g. of magnesium-free calcium chloride is weighed and dissolved in about 200 ml. of water. The solution is filtered. A 50-ml. portion of the filtrate is taken for the determination of CaO. A portion of the remaining filtrate is diluted so as to obtain a solution containing 0·1 mg. of CaO per ml.

MAGNESIUM.—Exactly 0·0604 g. of pure magnesium metal is weighed and dissolved in a small volume of hydrochloric or sulphuric acid. The solution is diluted to 1,000 ml. with distilled water. A 100-ml. portion of this solution is diluted to 1,000 ml. so as to obtain a solution containing 0·01 mg. of MgO per ml.

SODIUM.—Exactly 32·26 ml. of 0·1-N sodium hydroxide solution made of potassium-free p. a. NaOH is neutralized with an equal volume of 0·1-N hydrochloric acid and diluted to 1,000 ml. This solution contains 0·1 mg. of $Na_2O$ per ml.

POTASSIUM.—Exactly 21·28 ml. of 0·1-N potassium hydroxide solution made of sodium-free KOH is neutralized with an equal volume of 0·1-N hydrochloric acid and diluted to 1,000 ml. This solution contains 0·1 mg. of $K_2O$ per ml.

### Preparation of Sample Solutions.

The procedures for the preparation of the sample solutions are described in the following. Three sample solutions are required for a complete colorimetric analysis, that is, sample No. 1 for the determination of $Na_2O$ and $K_2O$; No. 2 for the determination of $SiO_2$, $Fe_2O_3$, $TiO_2$, and $Al_2O_3$; and No. 3 for the determination of MgO and CaO.

SAMPLE SOLUTION No. 1.—A dried and finely powdered 2-g. sample is weighed into a platinum dish and heated to 500 deg. C. to 600 deg. C. to destroy organic matter. After the sample has cooled, about 2 ml. of water are added, followed by 15 ml. of 40 per cent. hydrofluoric acid. All lumps are crushed by means of a platinum spatula, and the solution is evaporated to dryness on a hot plate. To

the residue is added 4 ml. of 3 : 1 $H_2SO_4$, and the sulphuric acid is fumed off until the sample is nearly dry.  The salt cake is transferred to a 150-ml. beaker, and about 50 ml. of water are added, while crushing with a glass rod.  The solution is heated to boiling, neutralized with ammonia to methyl red, and leached on a water bath for 30 minutes.  After leaching, the solution is filtered through a Jena 17 G4 glass filter, and the precipitate is washed with four 10-ml. portions of hot water. The filtrate is diluted to 200 ml. in a graduated flask.

SAMPLE SOLUTION NO. 2.—A dried and finely powdered 0·2-g. sample is ignited and thoroughly mixed with about 0·5 g. of potassium sodium carbonate in a platinum crucible.  This mixture is covered with about 0·25 g. of potassium sodium carbonate.  The lid is put on the crucible, and the crucible is heated over a small flame so that only its bottom is brought to red heat.  After ten minutes a change is made to a full Meker burner flame, and the sample ignited for a further period of 25 minutes. The crucible is allowed to cool, no measures being taken to accelerate the cooling.  When completely cool, the crucible is filled with water to two-thirds of its height, and its bottom is gently heated over a slight fluttering flame.  The whole melt can usually be detached from the wall of the crucible when the water begins to boil, otherwise the solution is poured out of the crucible and fresh water is added.  This procedure is repeated until the crucible is completely clean.  If necessary, the crucible is cleaned with a few drops of concentrated hydro-chloric acid.  The lid must also be cleaned.  The melt is crushed in a platinum dish and dissolved in 50 ml. to 100 ml. of water after adding 2 ml. of concentrated hydrochloric acid and a few drops of 3 per cent. hydrogen peroxide.  All lumps are thoroughly crushed.  The solution is boiled until the sediment consists only of pure white silicic acid, and the excess hydrogen peroxide has been evaporated.

The solution is filtered through a filter which should be as small as possible. The precipitate is washed very thoroughly in hot water containing a small amount of hydrochloric acid.  The filtrate and the wash water are transferred to a 1,000-ml. graduated flask containing about 400 ml. of water.  The filter is returned to the platinum dish and crushed in about 25 ml. of 1-N sodium hydroxide.  The solution is diluted to about 50 ml. and boiled.  After the solution has been boiling for five minutes, it is diluted by transferring it to a beaker containing about 350 ml. of water and neutralized with 25 ml. of 1-N hydrochloric acid.  The neutralized solution is filtered through a medium-sized filter.  The filter is thoroughly washed with one portion of water, then with a few drops of concentrated hydrochloric acid, and finally with several portions of hot water containing a small amount of HCl.

Both filtrates are poured into the same flask, allowed to cool to 20 deg. C., and diluted to 1,000 ml.  As this solution will not keep for long, the determination of silica must be made immediately.

SAMPLE SOLUTION NO. 3.—A dried and finely-powdered 0·5-g. sample is weighed into a platinum crucible, ignited, mixed with about 1·0 g. of potassium sodium carbonate, and then treated in the same way as the sample used for solution No. 2.  After the fusion is complete, the crucible is allowed to cool.  The

melt is dissolved in a small volume of water and 5 ml. of concentrated hydrochloric acid in a 250-ml. beaker. A few drops of 3 per cent. hydrogen peroxide are added to the solution. The solution is diluted to about 50 ml. Lumps are crushed with a glass rod. The solution is boiled until all substances except $SiO_2$ are dissolved, and a few drops of methyl red are added. If the sample contains manganese, more $H_2O_2$ must be added now and then during boiling.

Iron and aluminium are precipitated by neutralizing the solution with concentrated ammonia which is added drop by drop, while continually stirred. A few drops of ammonia are added in excess. The solution is filtered through a medium-sized filter. The filtrate is transferred to a 250-ml. graduated flask. The filter is crushed in the precipitation beaker in 5 ml. of concentrated HCl. The solution is diluted to about 50 ml. and brought to boiling. The precipitation procedure is repeated. The solution is filtered. The precipitate is washed with four portions of 2 per cent. ammonium chloride solution. The filtrate and the wash liquid are transferred to a 250-ml. graduated flask. Finally, the collected filtrates are slightly acidified, allowed to cool and diluted to 250 ml.

### Determination of $SiO_2$.

A sample containing from 1 mg. to 1·5 mg. of $SiO_2$ taken from a newly-made solution is diluted to 25 ml., if required, mixed with about 0·1 g. of $NaHCO_3$, covered with a glass lid, and heated on a boiling water bath. After heating for 15 minutes at least, the solution is neutralized with $H_2SO_4$ to phenolphtalein. The solution is transferred to a 100-ml. graduated flask and diluted with water to a total volume of about 75 ml. To this solution are added 5 ml. of concentrated HCl and 15 ml. of a 20 per cent. ammonium molybdate solution, and the sample is immediately diluted to 100 ml. After about one hour the intensity of colour of the sample solution is measured at a wave length of 436 m$\mu$.

### Determination of $Fe_2O_3$.

A sample containing less than 0·2 mg. of $Fe_2O_3$ is diluted with water to 50 ml. and acidified by adding 2 ml. of concentrated $HNO_3$ free from nitrous gases and nitrous acid. To this solution is added 0·2 ml. of 3 per cent. $H_2O_2$. After shaking, 15 ml. of a 20 per cent. KCNS solution are added. The sample is mixed and allowed to stand for 30 minutes. Finally, the solution is diluted to 100 ml. and the intensity of the colour is measured at a wave length of 546 m$\mu$.

### Determination of $TiO_2$.

To a 100-ml. sample solution containing less than 1 mg. of $TiO_2$ is added 0·3 ml. of 3 per cent. $H_2O_2$, followed by 5 ml. of concentrated $H_2SO_4$. The sample solution is thoroughly mixed and cooled to 20 deg. C. The intensity of the colour is measured at a wave length of 436 m$\mu$. The intensity of the colour of the sample is also measured after the addition of sulphuric acid only, without hydrogen peroxide, and a correction is made for the colour of the solution.

### Determination of $Al_2O_3$.

REAGENT SOLUTION.—40 ml. of glacial acetic acid are diluted to about 500 ml. and neutralized with 50 ml. of concentrated ammonia. To this mixture are

added 200 ml. of a 0·1 per cent. aluminon solution, and the solution is diluted to 1 litre. The quantity of 1N HCl that must be added to 100 ml. of reagent solution in order to obtain a pH of 5 is determined by potentiometric titration.

Aluminon is produced by adding slowly and in small portions while vigorously stirring 4 g. of sodium nitrite to 44 ml. of sulphuric acid (specific gravity 1·84) in a 250-ml. beaker. After the whole of the sodium nitrite has dissolved, the solution is cooled to 10 deg. C. Add 12 g. of salicylic acid during five to ten minutes while shaking the solution. Cool the solution to 3 deg. C. by embedding the beaker in crushed ice. Add drop by drop 3·5 ml. of about 35 per cent. solution of formaldehyde while vigorously stirring. The temperature must not exceed 5 deg. C. at this stage. When the whole of the formaldehyde has been added, allow the beaker to stand in an ice bath for about an hour, stirring the solution every five minutes. Cover the beaker and allow it to stand in an ice bath for 20 hours. Transfer the contents of the beaker into a vessel containing 2 litres of cold distilled water, while stirring vigorously. Allow the solution to stand for an hour. Filter through a Büchner funnel using 15-cm. filter paper of close texture. Wash the precipitate three times with distilled water, and pour it back into the beaker used for filtration. Add 1 litre of water and 50 ml. of hydrochloric acid (specific gravity 1·18), and boil for two to three minutes. Allow the precipitate to stand for ten minutes and wash it three times with water by decanting. Crush and remove the black mass by means of a stirring rod flattened at one end. Repeat twice the boiling with 1 litre of water and 50 ml. of hydrochloric acid and the subsequent washing with water as already described. Dissolve the residue in an excess of ammonium hydroxide. Evaporate the solution to dryness on a steam bath. Allow the residue to cool, grind to a fine powder, and keep in a stoppered bottle until required.

PROCEDURE.—A sample containing 0·15 to 0·55 mg. of $Al_2O_3$ is mixed in a 150-ml. beaker with a suitable quantity of iron solution so as to bring the $Fe_2O_3$ content of the sample to 0·300 mg. The solution is neutralized with 1N sodium hydroxide to phenolphtalein. The quantity of 1N HCl determined from the buffer curve of the reagent solution is added. The solution is diluted to 100 ml. Into a 250-ml. graduated flask is measured 100 ml. of reagent solution. The sample solution, corrected for iron and acidified, is transferred into the flask. The beaker used for the sample solution is carefully rinsed. The solution is diluted to 250 ml. and thoroughly mixed. The graduated flask is immersed in a boiling-water bath to such a depth that only the neck of the flask is out of the water bath. After 60 minutes the solution is cooled to 19 deg. to 20 deg. C. The intensity of the colour is measured at a wave length of 546 m$\mu$.

The measurement must be made so rapidly that the sample is not heated in the colorimeter to a temperature exceeding 20 deg. C. All vessels before use should be meticulously cleaned with concentrated nitric acid.

## Determination of MgO.

A 10-ml. sample solution is diluted to 100 ml. A portion of this solution containing about 0·1 mg. of MgO is transferred to a 150-ml. beaker, diluted to

50 ml., and mixed with 10 ml. of a reagent solution containing 25 g. of saccharose, 10 g. of hydroxylamine hydrochloride, and 0·2 g. of CaO per litre. The solution is allowed to stand for a few minutes, and 20 ml. of 1N NaOH are added. The sample solution is allowed to stand for 60 minutes and is transferred to a 100-ml. graduated flask containing 15 ml. of titan yellow solution. The sample solution is diluted to 100 ml. The colour intensity is measured immediately at a wave length of 546 m$\mu$. The titan yellow solution is made by dissolving 0·2 g. of titan yellow in 60 per cent. alcohol and diluted with equally strong alcohol to 1,000 ml. The solution is mixed with 500 ml. of 1N NaOH and kept in a dark bottle sealed with paraffin wax.

## Determination of CaO.

To 50 ml. of the sample solution (at high CaO contents the volume of the sample should be reduced to 25 ml. diluted with water to 50 ml.) are added 25 ml. of saturated ammonium oxalate solution and a few drops of methyl red, followed by hydrochloric acid until an acid reaction is obtained. The solution is neutralized with concentrated ammonia added drop by drop, with stirring. A few drops of ammonia are added in excess. Next 25 ml. of 96 per cent. alcohol are added, and the sample solution is allowed to stand for 10 minutes. The sample solution is brought to boiling, filtered while hot through a Jena 3 G4 glass filter, and thoroughly washed with warm wash liquid consisting of 1 part of alcohol and three parts of water. The precipitate and the precipitation beaker are dried in an oven at 105 deg. C. for ten minutes. The dry precipitate is then dissolved in 50 ml. of warm 1 : 4 sulphuric acid. The precipitation beaker is thoroughly rinsed at the same time. The filter and the beaker are washed four or five times with hot water. The sample solution is diluted with boiling water to about 200 ml., about 10 ml. of a 5 per cent. manganous sulphate solution are added, and the sample solution is titrated with 0·1N potassium permanganate solution.

## Determination of Na$_2$O.

A measured volume, say 5 ml., of the sample solution is transferred to a platinum dish, with 1 ml. of 10 per cent. CaCl$_2$ solution, and evaporated to dryness. The ammonium salts are carefully fumed off by gentle ignition. The solution contains $(H_4N)_2SO_4$, which cannot be removed from the residue remaining after evaporation by fuming off since it decrepitates under heat. If $(H_4N)S_2O_4$ is converted by means of CaCl$_2$ into H$_4$NCl and CaSO$_4$, the ammonium salts can readily be fumed off. The residue is dissolved in 1 ml. of 1 : 10 acetic acid, and 10 ml. of zinc uranyl acetate solution are added. The sample solution is allowed to stand for two hours, with stirring at intervals, and is filtered through a Jena 3 G4 glass filter funnel. The precipitate is washed with three 5-ml. portions of wash-alcohol. The wash-alcohol consists of 1 part of 96 per cent. alcohol and 4 parts of 96 per cent. alcohol saturated with triple acetate. The precipitation beaker is also washed the first two times. The alcohol is drawn off by suction, and the filter funnel is placed into a clean filtering flask. The precipitate is dissolved in hot water by suction, and the precipitation beaker is rinsed out with the solvent water. The total volume of the solution should be about 150 ml.

The solution is transferred to a 250-ml. graduated flask and cooled to about 20 deg. C. To this solution are added 10 ml. of the ammonium carbonate solution, followed by 10 ml. of a 3 per cent. hydrogen peroxide solution. Finally, the sample solution is diluted to 250 ml. and allowed to stand for 25 minutes. The intensity of the colour is measured at a wave length of 436 m$\mu$.

### Determination of K$_2$O.

A 5-ml. sample solution mixed with 1 ml. of 10 per cent. CaCl$_2$ solution is evaporated to dryness in a platinum dish. The ammonium salts in the residue are carefully fumed off as described for Na$_2$O. The residue is dissolved in 1 ml. of dilute acetic acid 1 : 10, while crushing the salt cake. The insoluble remainder, if any, is not filtered off. Then 10 ml. of platinic chloride solution (10 mg. Pt per ml.) are added and the solution is evaporated to dryness on a water bath. The residue after evaporation is dissolved in 10 ml. of 96 per cent. alcohol. The solution is filtered through a Jena 3 G4 glass filter funnel. The precipitate is washed with four 10-ml. portions of absolute alcohol saturated with potassium chloroplatinate. The platinum dish is also thoroughly rinsed at the same time. The filter funnel and the platinum dish are dried in an oven at 105 deg. C. for ten minutes. The glass filter funnel is put into a clean filtering flask. The precipitate is dissolved in 25 ml. of 1 : 1 hydrochloric acid and rinsed four times with boiling water. The precipitation dish is also carefully rinsed every time. The solution is transferred to a 200-ml. graduated flask, mixed with 25 ml. of 5 per cent. solution of potassium iodide, cooled, and diluted to 200 ml. After the solution has stood for 60 minutes, the intensity of the colour is measured at a wave length of 546 m$\mu$ or 436 m$\mu$.

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### German Cement Patents.

THE German Division of the Technical Information and Documents Unit of the Board of Trade (38/46, Cadogan Square, London, S.W.1), has photostat copies of claims for patent rights filed by the Portlandzementwerk Dotternhausen, Rudolf Rohrbach K.G., Stuttgart-N, relating to hydraulic cement binders manufactured principally from oil shale or oil shale residues after the shale has been subjected to hydrothermal treatment. There are seven claims, each accompanied by a condensed translation in the English language. In general, it is claimed that the processes described produce binders which do not suffer from the drawbacks hitherto inherent in the use of oil shale or its residues, and that the resulting cement is equal to the highest grade standard cement. Copies of these claims will be supplied by arrangement with the Board of Trade at the address given above

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# Effect of Alkalis on the Phase Composition of Clinker.

SOME of the preliminary investigations in an examination of the quinary system $Na_2O$-$CaO$-$Al_2O_3$-$Fe_2O_3$-$SiO_2$, undertaken by Mr. William R. Ewbank and Mr. Robert H. Bogue, are reported in Research Paper No. 1867 of the United States Bureau of Standards.

In a summary of the report it is stated that in the investigations $SiO_2$ and $Al_2O_3$ were not present together in any of the compositions studied. The purpose was to provide the necessary information preliminary to the extension of the studies to the quinary system N-C-A-F-S. The work has revealed that the extension of the field of CaO due to the introduction of $Na_2O$ applies also in the systems and regions covered in the present study. Also, the presence of soda was observed to lower the temperature of formation of the first liquid. However, the influence of soda on the burnability of Portland cement clinker cannot be stated with assurance until the simultaneous phase-equilibrium relations of all five components have been completed. Likewise, the nature of the soda phase in Portland cement clinker cannot be stated with assurance until the completion of the quinary system. At the present state of information it appears that the phase $NC_8A_3$ is stable over a wide range and probably constitutes the principal soda phase in clinker, although soda has been observed to enter into several different solid solutions. It is possible that this phase may interact with calcium sulphate, as was found to be the case with the potash compound $KC_{23}S_{12}$.

It has previously been shown that soda enters into solid solution with $\alpha$ $C_2S$ following interaction with $C_3S$ by which CaO is liberated. When the $\alpha$ $C_2S$ solid solution inverts to the $\beta$ form on cooling, the soda appears to be precipitated, perhaps as $NC_8A_3$, and to remain as inclusions in the crystallized silicate grains. Further evidence of this reaction was obtained in the present study, where the $C_2S$ phase was observed in all three of its polymorphic forms. Soda-containing charges that were rapidly quenched from 1,300 deg. C. or above were sometimes observed to contain $\alpha$ $C_2S$, characterized by its glassy appearance and $\alpha$ index close to 1·713. The crystals in many cases were found to contain very fine dark inclusions. The $\alpha$ to $\beta$ inversion temperature was found to be lowered from 1,456 deg. C., as reported by Newman and Wells, by as much as 156 deg. The $\beta$ form of $C_2S$, readily identified by its twinned structure, was found in slowly-cooled clinker. These crystals contained inclusions of fairly large rounded grains that are believed to be due to the exsolution of a soda-containing phase. The slowly-cooled charges contained considerable amounts of $\gamma$ $C_2S$, and often dusted due to the inversion of the $\beta$ $C_2S$ to the gamma form.

Occasionally, in charges of high-iron concentration, small areas of brighter colour and higher birefringence were observed in the dark-brown glass surrounding the grains of dicalcium silicate. It appears probable that these areas are caused

by an interaction of the soda (coming out of solution in the $C_2S$) with the surrounding glass.

The petrologic significance of certain ternary subsystems in the high-silica portion of the system N-C-A-S- has recently been reported by Goldsmith. Although these investigations consider concentrations of silica much higher than those encountered in that study, certain relations such as those of solid solution appear to be similar. The predominance of solid solutions in these systems is worthy of note. It was stated that the only substantially pure phase existing either in natural magmas or synthetic melts in this range of compositions is the mineral quartz. All other phases exist in some form of solid solution. A similar situation seems to exist in the systems under consideration here. In this case it is likely that the only pure phase encountered is free CaO, the remaining phases reacting with each other to a greater or lesser extent to form solid solutions.

Certain of these solid solutions may be defined only in terms of the oxide components of the large quaternary system N-C-A-S. In other words, ternary subsystems having various compounds such as $C_4AF$ or $C_5A_3$ as components may be nonternary. That is, phases encountered are not capable of being expressed in terms of the end members of the ternary system considered, and liquids formed upon crystallization of solid solutions fall outside that ternary system in composition. One reason for this appears to arise from the nature of these solid solutions, in which solution takes place in the form of the smaller oxide units rather than the larger ones involving compounds.

At the liquidus such systems may behave as ordinary ternary systems, but below the liquidus the composition of both solid solutions and liquids is usually outside the given plane. Courses of crystallization cannot be traced readily, and the phase-equilibrium relations in general increase in complexity in systems containing solid solutions.

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### The Chinese Cement Industry.

The Board of Trade informs us that the Minister (Commercial) at Shanghai has written a report on "The Chinese Cement Industry during the year 1947." A copy of the report is available for inspection at the Export Promotion Department (Room 1112), Board of Trade, Thames House North, Millbank, London, S.W.1. The report states that in China a very high-grade cement is made, and that the industry may eventually be able to meet the whole of China's internal requirements. Nevertheless, the potential demand is very large and it remains to be seen whether the cement production programme can meet the demand. In addition information is available regarding a visit to the Taiwan cement works at Takao, which is described as the largest in China. A recent announcement in the "China Daily Tribune" stated that to encourage China's cement production the Government has banned the import of foreign cement.

# Proportioning Raw Materials for Portland Cement

IN a series of articles in " Rock Products " in 1947, Mr. L. A. Dahl considers the problem of the proportioning of the mixtures of the raw materials for Portland cement. The bases of rapid methods for controlling the mixture are discussed with particular reference to the amount of carbonate required to ensure a suitable content of $C_3S$ and $C_2S$. The carbonate content ($CaCO_3$ + 1·19 $MgCO_3$) is obtained from the amount of acid neutralised, or $CO_2$ liberated, by a sample of the mixture. An analysis of the mixture enables the compound composition of the clinker to be calculated. If the change in the composition of the raw material is gradual, the selected " holding point " may be frequently adjusted (as indicated by changes in the carbonate requirement) so as to maintain a constant potential amount of $C_3S$ or $C_2S$. There is, however, always a lag in control due to the time between proportioning the materials and the determination of the carbonate content. Increasing the carbonate content by 1 per cent. increases the potential content of $C_3S$ by about 14·5 per cent. and decreases the potential content of $C_2S$ by about 13·5 per cent. From these data an equation is evolved for determining the carbonate requirement for a particular mixture. The influences of coal ash, of dust losses, and of changes in the composition of the limestone, such as variations in the amount of magnesia and the loss on ignition, are also considered. A quantitative method of controlling the carbonate requirement so as to allow for the effects of small additions of iron ore and sand in the production of low-heat or sulphate-resistant cement is explained.

The application of the determinations of the carbonate requirement to the control of the composition of the raw mixtures is fully described for continuous and two-stage methods of proportioning. In the continuous method the crushed raw materials are proportioned, ground, and then blended to equalise variations in composition by filling the silos consecutively and emptying them simultaneously. The changes to be made to maintain a constant $C_3S$ or $C_2S$ content may be effected either by assessing the carbonate requirement in the proportioning operation or, when this requirement varies too rapidly, by assessing it in the blending operation, since it is then only necessary that the average carbonate content should coincide with the average carbonate requirement. In the two-stage method, which is commonly used in the wet process, the materials are approximately proportioned and, after grinding and batching, are again proportioned when in the form of slurry. The carbonate requirement is finally adjusted by control of the carbonate content from the analysis of each tank of slurry during the second proportioning operation. The foregoing notes are taken from " Building Science Abstracts."

# Revision of the American Standard Specifications for Cement.

SEVERAL revisions were made in 1947 in the standard specifications for various kinds of cement by the American Society for Testing Materials, and the latest specifications and methods of testing are included in " A.S.T.M. Standards on Cement, with related Information," published in 1948 by the Society (price 2 dollars). The principal alterations are given in the following.

The specifications for Portland cements (C150—47) were revised in 1946 as regards the contents of sulphur-trioxide (see this journal for September, 1946), and now the calculated maximum content of tricalcium-silicate in Portland cement having a high-sulphate resistance (Type V) is specified as 50 per cent., which is the same as that for cement (Type II) for use in general concrete construction exposed to moderate sulphate action or where a moderate heat of hydration is required.

The tentative specification (C175-47T) for air-entraining Portland cement was revised again in 1947 when the air-content of mortar prepared and tested in accordance with the tentative method (C185-1947) was increased to 18 per cent. ± 3 per cent. Some alterations were made in the dimensions and descriptions of the straightedge, spatula, mixing bowl, and the Burmister mortar-flow troughs used for this test ; the tamping rod is not now required.

A note is now included in the tentative specification for Portland blastfurnace-slag cement (C205-47T) that a proprietary compound, composed of triethanolamine and highly purified soluble calcium salts of modified lignin sulphonic acids, is not considered as a harmful addition if the amount does not exceed 0·08 per cent. (by weight) of the cement.

In the chemical analysis of Portland cement (C114-47) the primary methods of determining the amount of the principal constituents are now called " referee methods," and the shorter and more convenient methods described as " alternate methods " are now called " optional methods." A referee method must be used where an optional method is not described, and a cement can only be rejected for failure to comply with a chemical requirement if tested by a referee method, the determination being made in duplicate and the analyses made on two different days. If the results of the two determinations do not agree within certain permissible variations, the determination must be repeated until two, or three, results agree within the permissible variation, and the average of such results must be accepted as the correct value. The permissible variations between two results are given in the following, and the permissible variation between the extreme values of three results is 50 per cent. greater : $SiO_2$ and MgO, 0·16 ; $Al_2O_3$, CaO, and free CaO, 0·20 ; $Fe_2O_3$, $SO_3$, loss on ignition, and insoluble residue, 0·10 ; $Na_2O_3$, $K_2O$, $P_2O_5$, and $Mn_2O_3$, 0·03 ; water-soluble alkali, 0·05 ; and chloroform-soluble organic substances, 0·004. For comparison of analyses and for the calculation of average results, the percentage must be calculated to the nearest 0·01 (or 0·001 for chloroform-soluble organic substances), although

some of the average values are reported to the nearest 0·1. Alterations, some only slight, have been made in the descriptions of the referee methods for the determination of $SiO_2$, the ammonium hydroxide group, $Fe_2O_3$, $Al_2O_3$, MgO, $SO_3$, and chloroform-soluble organic substances. In the " alternate " or " optional " methods, alterations have been made in the description of the methods of determining $SiO_2$, CaO, and MgO.

The descriptions of the flow-table test and the method of moulding the specimens for the determination of the compressive strength of cement mortar (C109-47) have been altered to include the tentative revisions appended to the 1944 edition of this Standard.

The tentative method of determining the heat of hydration of Portland cement, which was issued in 1944, has now been adopted as a standard method (C186-47). The calorimeter and the method of calculation are similar to those described in the British Standard (see this journal for March, 1948).

STANDARDS UNALTERED.—Current specifications for cements other than those mentioned in the foregoing, and which were not revised in 1947, are the standard specifications for natural cement (C10-1937) and masonry cement (C91-1940) and tentative specification C91-1944.

The methods of testing which were not altered in 1947 are the autoclave test for the expansion of Portland cement (C151-1943) ; tentative methods of chemical analysis of Portland cement (C114-1946T) ; fineness of hydraulic cement by sieve No. 200 (C184-1944) ; tentative method of test for the fineness of Portland cement by the air-permeability apparatus (C204-1946T)—this is the Blaine apparatus which comprises a manometer and permeability cell that differ in detail from the apparatus used in the British standard test described in our number for March, 1948 ; fineness test for Portland cement by the Wagner turbidimeter (C115-42) ; normal consistency of hydraulic cement (C187-1944) ; sampling hydraulic cement (C183-1946) ; soundness of hydraulic cement in the boiling water (pat) test (C189-1944) ; specific gravity of hydraulic cement (C188-1944) ; tensile strength of hydraulic cement mortars (C190-1944) ; and the time of setting of hydraulic cement determined by the Vicat apparatus and by the Gillmore needle (C191-1944).

## German Cement-making Plant.

INFORMATION is available at the German Division (Documents Unit) of the Board of Trade, 38 Cadogan Square, London, S.W.1, on the cement-making plant made by Kloeckner-Humboldt-Dentz, A.G., of Cologne. The material available, in addition to notes in the English language, includes drawings giving details of this firm's coal-grinding machines, the Colombus mill, a tubular grinding mill, a cylindrical drying separator, a flotation process, a coal flotation machine, a wet separator drum, automatic furnaces (Mannstead system), a shaft kiln, and a compound mill. The drawings give the general arrangement and details of the machines. The information may be inspected by those interested ; applications for permission to do so should quote the reference FD5480/47.

## Cement-making Machinery

A brochure illustrating some of the production methods used in the manufacture of cement kilns, crushers, grinding mills, coolers and other plant used in the manufacture of cement has been issued by Vickers-Armstrongs, Ltd., of Barrow-in-Furness. This company makes all classes of cement-making machinery, and since this department was re-opened in 1945 orders have been received from France, Mexico, India, the Near East, South Africa and other countries abroad, as well as for cement works in Britain.

## Cement from Germany.

Arrangements are being made for the import from Germany of cement and cement clinker to augment the supplies in areas normally supplied with British cement. The first deliveries will go to Scottish ports. The German cement will be sold in Scotland by the Cement Marketing Co., Ltd., and the clinker will be used by the Clyde Portland Cement Co., Ltd., and the Caledonian Portland Cement Co., Ltd. The cements will comply with British standards.

## MISCELLANEOUS ADVERTISEMENTS

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SITUATIONS VACANT. Staff required by Government of Ceylon for Cement Factory, Kankesanturai, in course of construction. Chief Engineer. Salary £1,000 per annum fixed. Appointment probably December 1948. Five years' agreement. Candidates, aged 40-45, should have good practical training in general mechanical engineering, and be familiar with chemical engineering. Should have sound practical training in cement works' operation and maintenance, including stone quarrying experience. In general should be capable of acting as manager if necessary. Should also have power-station knowledge as it will be necessary to interchange with power station engineer.

Chief Chemist. Salary £900 per annum fixed. Appointment probably September 1948. Five years' agreement. Candidates, aged 35-45, should have sound chemical training and be competent in organic analysis, with knowledge of physics and, if possible, physical chemistry; must have practical cement works' experience and complete knowledge of uses of cement as he may have to answer questions on this subject from clients and investigate complaints.

Two Burners. Salary £600 per annum fixed. Appointment probably February 1949. Five years' agreement. Candidates, aged 35-50, must have had long experience in rotary-kiln burning by wet and dry processes, preferably with knowledge of oil and coal firing equipment, and be capable of taking over from chief burner as required.

Cost of living allowance Rs.70 a month payable in all cases. Posts are non-pensionable, but provident fund exists. Possibility that agreements may be renewed. Government quarters provided at rental of 6% of salary; free passages out and home for officers and families; leave, travelling allowance, etc., in accordance with regulations. Apply at once by letter stating, age, whether married or single, and giving full particulars of qualifications and experience, and mentioning this paper, to the Crown Agents for the Colonies, 4, Millbank, London, S.W.1, quoting M/N/21442/3E on both letter and envelope.

FOR SALE. Cement briquette-testing machines (by Bailey and Faija). 10 guineas each. Pattison, 200, Siddals Road, Derby (45249).

FOR SALE. Plan now for 1949 season. We offer Powel-Hill concrete roofing tile machines for sale. Modern and completely reconditioned. Large production type. Pattison, 200, Siddals Road, Derby (45249).